

## Application Note

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### Abstract

US EPA Method 524.4 is used primarily by environmental labs for the analysis of volatile organic compounds (VOCs) in drinking water. While this method is effective at concentrating the trace levels of VOCs sometimes found in finished drinking water, it also tends to transfer significant quantities of water vapor to the gas chromatography-mass spectrometry instruments.

Teledyne Tekmar's Lumin purge and trap (P&T) concentrator incorporates a moisture control system (MCS) specifically designed to reduce the amount of water transferred during desorb, in comparison to current purge and trap technologies. This application note will demonstrate the ability of the Lumin to reduce the amount of water transferred to the Thermo Scientific GC-MS system when using this method.



### Introduction

Gas chromatography (GC) inlets, columns and mass spectrometers (MS) are sensitive to water. However, to detect toxic VOC compounds, the VOCs must be purged and trapped from water. This places water vapor on the GC-MS system, which contributes to column and inlet issues and frequent MS cleaning to remove the oxidation from the MS source.

US EPA Method 524.4 places a large amount of water vapor on the GC-MS system. This method allows flexibility in the dry purge and desorb time of the analytical trap to reduce the large volumes of water that inundate the GC-MS system and lead to poor chromatography for early eluting gases. It also allows the use of nitrogen for the purge gas.

Traditionally, purge and trap instruments reduced the amount of water transferred to GC-MS instrument through numerous water management techniques. The Teledyne Tekmar Lumin significantly reduces the amount of water transferred to the GC-MS system over current P&T instrumentation, through the design of its MCS. Additionally, improvements in analytical trap cooling have further reduced sample cycle times, permitting more samples to be processed within a 12-hour period.

### Sample Preparation

Calibration standards were prepared from Restek® 524.3 VOA MegaMix® and 524.3 Gas Calibration Mix standards in deionized water containing the required amount of maleic acid and ascorbic acid. A calibration curve was prepared from 0.2 ppb to 50 ppb for all of the compounds.

The relative response factor (RF) was calculated for each VOC using either 1,4-difluorobenzene, chlorobenzene-d5 or 1,4-dichlorobenzene-d4 as an internal standard. Surrogate standards consisted of: methyl-t-butyl ether-d3, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4. A linear calibration curve with 1/X weighting was used for all compounds.

Seven 0.5 ppb standards were prepared to calculate the method detection limit (MDL), accuracy and precision data. All calibration and MDL samples were analyzed with the Lumin and AQUATEk 100 conditions in [Table I](#) and the GC-MS conditions in [Table II](#).

The correlation coefficient of the calibration curve ( $r^2$ ), MDL, accuracy and precision data are shown in [Table III](#). A 0.2 ppb standard was analyzed to indicate the lowest detectable peak for the initial seven gases unencumbered by excessive water in [Figure 1](#). [Figure 2](#) displays a 5 ppb standard, indicating excellent peak resolution for all of the VOCs.

## Experimental Instrument Conditions

Table I Lumin and AQUATek 100 Conditions			
Standby	Variable	Bake	Variable
Valve Oven Temp	150 °C	Bake Time	2.00 min
Transfer Line Temp	160 °C	Bake Temp	260 °C
Sample Mount Temp	90 °C	MCS Bake Temp	180 °C
Purge Ready Temp	35 °C	Bake Flow	200 mL/min
MCS Purge Temp	20 °C	<b>AQUATek 100</b>	<b>Variable</b>
Standby Flow	20 mL/min	Sample Loop Time	0.35 min
<b>Purge</b>	<b>Variable</b>	Sample Transfer Time	0.35 min
Purge Time	11.00 min	Rinse Loop Time	0.30 min
Purge Flow	40 mL/min	Sweep Needle Time	0.30 min
Dry Purge Temp	20 °C	Presweep Time	0.25 min
Dry Purge Time	0 min	Water Temp	90 °C
Dry Purge Flow	0 mL/min	Bake Rinse Drain Cycles	3
<b>Desorb</b>	<b>Variable</b>	Bake Rinse Drain Time	0.35 min
Desorb Preheat Temp	245 °C		
Desorb Time	1.20 min	<b>Trap</b>	9
Desorb Temp	250 °C	<b>Chiller Tray</b>	On
Drain Flow	300 mL/min	<b>Purge Gas</b>	Nitrogen

Table II Thermo Scientific TRACE 1310 GC and ISQ LT MS System Conditions	
Thermo Scientific TRACE 1310 GC with Split/Splitless Instant Connect Injector Conditions	
Column	Rtx®-VMS, 20 m x 0.18 mm ID, 1 µm Film; Helium – 0.8 mL/min
Oven Profile	35 °C, 2 min, 10 °C/min to 100 °C, 25 °C/min to 225 °C, 2 min hold; Run Time 15.5 min
Inlet	200 °C, 65:1 Split, P&T Adapter, Gas Saver Flow - 20 mL/min after 1 min
Thermo Scientific ISQ LT MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 300 °C
Scan	Range 35 amu to 260 amu, Time 0.2 sec; Delay 0.8 min
Current	Emission Current 25 µA, Gain 3 e 5

## Results

Table III Method 524.4 Calibration, Accuracy and Precision Data

Compound	Calibration		MRL Confirmation (0.5 ppb)		Accuracy and Precision (n=7, 0.5 ppb)		
	Linearity (r <sup>2</sup> )	MDL (ppb)	LPIR (> 50%)	UPIR (<150%)	Avg. Conc. (ppb)	Accuracy (± 20%)	Precision (≤ 20%)
Dichlorodifluoromethane	0.993	0.11	60.1	114.3	0.44	87	7.8
Chlorodifluoromethane	0.997	0.12	66.6	127.9	0.49	97	8.0
Chloromethane	0.998	0.13	64.7	132.0	0.49	98	8.6
Vinyl Chloride	0.997	0.12	66.6	129.3	0.49	98	8.1
1,3-Butadiene	0.999	0.08	82.1	123.3	0.51	103	5.1
Bromomethane <sup>1</sup>	0.998	0.06	79.7	109.4	0.47	95	3.9
Trichlorofluoromethane	0.998	0.08	78.9	120.1	0.50	99	5.2
Diethyl Ether	1.000	0.09	79.6	125.5	0.51	103	5.7
1,1-Dichloroethene	0.998	0.09	73.7	118.7	0.48	96	5.9
Carbon Disulfide	0.997	0.08	77.1	118.8	0.49	98	5.4
Iodomethane	0.999	0.07	80.6	117.6	0.50	99	4.7
Allyl Chloride	0.999	0.10	73.6	122.5	0.49	98	6.3
Methylene Chloride	0.997	0.03	81.4	97.9	0.45	90	2.3
trans-1,2-Dichloroethene	0.998	0.08	71.1	109.0	0.45	90	5.3
Methyl Acetate	1.000	0.09	83.4	129.9	0.53	107	5.5
Methyl-t-Butyl Ether-d3 (Surr)	2.7 <sup>2</sup>				12.73	102	1.9 <sup>3</sup>
Methyl-t-Butyl Ether (MtBE)	1.000	0.04	94.1	116.0	0.53	105	2.6
t-Butyl Alcohol (TBA)	0.999	0.18	51.2	140.7	0.48	96	11.8
Diisopropyl Ether (DIPE)	0.999	0.04	90.1	110.3	0.50	100	2.6
1,1-Dichloroethane	0.999	0.06	78.9	110.8	0.47	95	4.2
t-Butyl Ethyl Ether (EtBE)	0.999	0.04	89.9	108.9	0.50	99	2.4
cis-1,2-Dichloroethene	0.999	0.09	77.2	120.6	0.49	99	5.6
Bromochloromethane <sup>4</sup>	1.000	0.05	90.3	114.9	0.51	103	3.0
Chloroform	0.998	0.09	69.4	112.9	0.46	91	6.1
Carbon Tetrachloride	0.999	0.13	64.7	128.7	0.48	97	8.4
Tetrahydrofuran	0.999	0.12	62.7	122.9	0.46	93	8.2
1,1,1-Trichloroethane	0.999	0.05	78.0	105.0	0.46	92	3.8
1,1-Dichloropropene	0.999	0.08	80.9	119.9	0.50	100	4.9
1-Chlorobutane	1.000	0.07	79.1	112.2	0.48	96	4.4
Benzene	1.000	0.06	81.0	111.2	0.48	96	4.0
t-Amyl Methyl Ether (TAME)	0.999	0.06	85.8	116.1	0.50	101	3.8
1,2-Dichloroethane	0.999	0.07	82.2	118.2	0.50	100	4.5
Trichloroethene	1.000	0.06	73.3	105.7	0.45	89	4.6
1,4-Difluorobenzene (IS 1)	8.1 <sup>2</sup>						4.9 <sup>3</sup>
t-Amyl Ethyl Ether (TAEE)	0.999	0.05	81.5	108.9	0.48	95	3.6

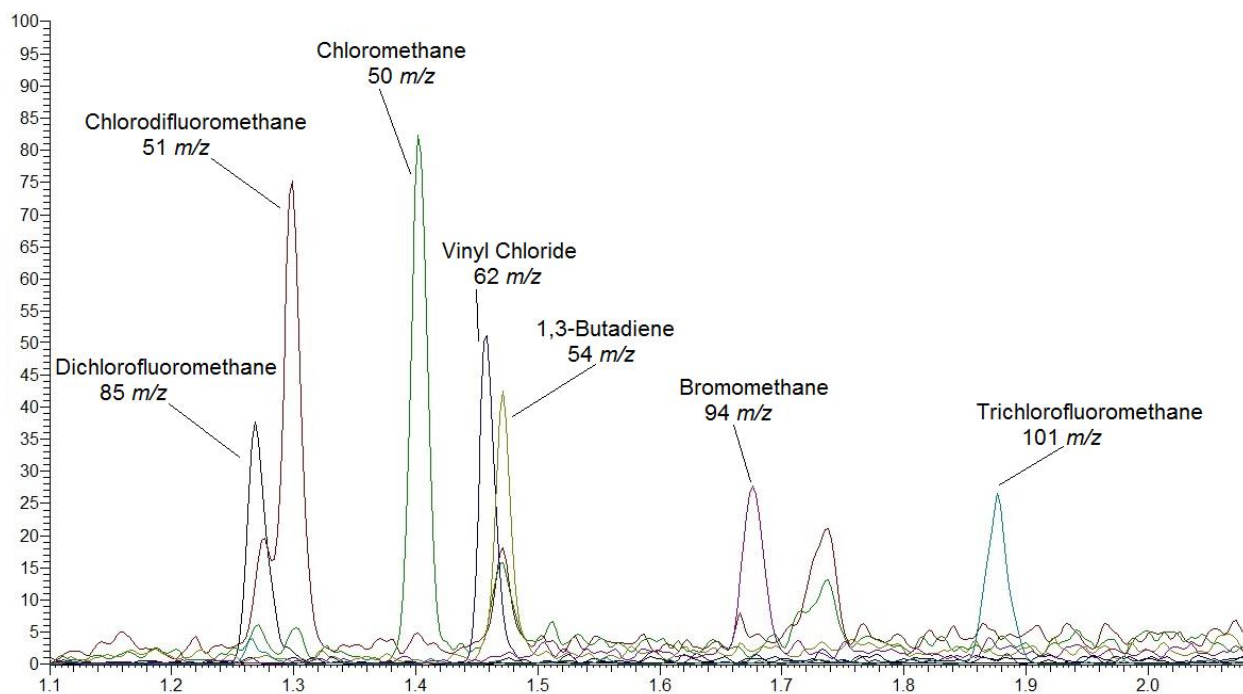
Table III Method 524.4 Calibration, Accuracy and Precision Data

Compound	Calibration		MRL Confirmation (0.5 ppb)		Accuracy and Precision (n=7, 0.5 ppb)		
	Linearity (r <sup>2</sup> )	MDL (ppb)	LPIR (> 50%)	UPIR (<150%)	Avg. Conc. (ppb)	Accuracy (± 20%)	Precision (≤ 20%)
Dibromomethane	1.000	0.09	78.3	125.4	0.51	102	5.8
1,2-Dichloropropane	1.000	0.05	86.7	109.7	0.49	98	3.0
Bromodichloromethane	1.000	0.05	82.3	108.0	0.48	95	3.4
cis-1,3-Dichloropropene	0.999	0.03	97.2	112.9	0.53	105	1.9
Toluene	0.999	0.06	82.8	112.0	0.49	97	3.7
Tetrachloroethene	0.999	0.07	68.9	103.1	0.43	86	5.1
trans-1,3-Dichloropropene	0.998	0.04	92.2	112.2	0.51	102	2.5
1,1,2-Trichloroethane	1.000	0.07	77.9	112.9	0.48	95	4.6
Ethyl Methacrylate	0.997	0.09	77.9	122.7	0.50	100	5.7
Dibromochloromethane	0.999	0.10	63.2	115.0	0.45	89	7.3
1,3-Dichloropropane	1.000	0.04	93.9	112.2	0.52	103	2.3
1,2-Dibromoethane (EDB)	1.000	0.06	84.0	115.1	0.50	100	3.9
Chlorobenzene-d5 (IS 2)	5.6 <sup>2</sup>						5.8 <sup>3</sup>
Chlorobenzene	1.000	0.09	74.9	118.9	0.48	97	5.8
Ethylbenzene	0.999	0.05	80.6	107.3	0.47	94	3.6
1,1,1,2-Tetrachloroethane	0.999	0.12	56.0	117.0	0.43	87	8.9
m- , p-Xylene	1.000	0.12	78.1	107.1	0.93	185	4.0
o-Xylene	0.999	0.09	71.5	116.7	0.47	94	6.1
Styrene	0.998	0.04	87.4	108.9	0.49	98	2.8
Bromoform	0.998	0.06	80.6	111.4	0.48	96	4.1
Isopropylbenzene	0.999	0.09	70.5	114.7	0.46	93	6.0
4-Bromofluorobenzene (Surr)	2.2 <sup>2</sup>				12.31	98	2.2 <sup>3</sup>
Bromobenzene	0.999	0.08	76.3	114.9	0.48	96	5.1
Propylbenzene	0.999	0.05	78.8	105.8	0.46	92	3.7
1,1,2,2-Tetrachloroethane	0.998	0.08	75.5	114.1	0.47	95	5.2
2-Chlorotoluene	0.999	0.10	63.9	115.3	0.45	90	7.2
1,3,5-Trimethylbenzene	1.000	0.12	70.4	129.8	0.50	100	7.5
1,2,3-Trichloropropane	0.999	0.05	77.6	102.8	0.45	90	3.5
4-Chlorotoluene	0.999	0.04	84.5	103.4	0.47	94	2.5
tert-Butylbenzene	0.999	0.19	54.3	147.5	0.50	101	11.6
Pentachloroethane <sup>1</sup>	0.998	0.09	71.9	115.3	0.47	94	5.8
1,2,4-Trimethylbenzene	0.999	0.05	76.5	101.7	0.45	89	3.5
sec-Butylbenzene	0.999	0.04	79.4	100.1	0.45	90	3.0
4-Isopropyltoluene	0.999	0.07	70.9	107.0	0.44	89	5.2
1,3-Dichlorobenzene	1.000	0.06	76.6	104.3	0.45	90	3.9
1,4-Dichlorobenzene-d4 (IS3)	5.7 <sup>2</sup>						4.6 <sup>3</sup>

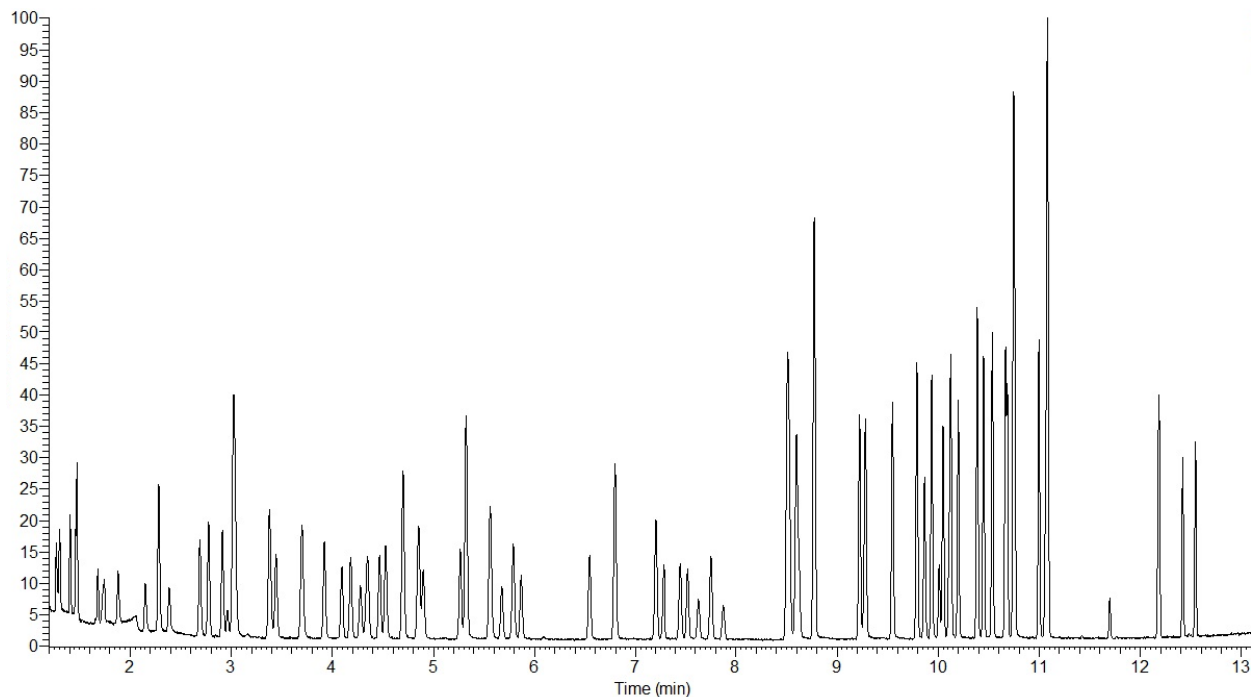
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	Linearity (r <sup>2</sup> )	MDL (ppb)	LPIR (> 50%)	UPIR (<150%)	Avg. Conc. (ppb)	Accuracy (± 20%)	Precision (≤ 20%)
1,4-Dichlorobenzene	1.000	0.06	78.3	105.7	0.46	92	3.8
Butylbenzene	0.997	0.09	71.0	115.5	0.47	93	6.0
Hexachloroethane	1.000	0.16	51.8	133.8	0.46	93	11.1
1,2-Dichlorobenzene	1.000	0.08	74.1	112.4	0.47	93	5.1
1,2-Dichlorobenzene-d4 (Surr)	3.2 <sup>2</sup>				12.75	102	2.3 <sup>3</sup>
1,2-Dibromo-3-chloropropane	0.998	0.05	85.4	112.4	0.49	99	3.5
Hexachlorobutadiene	0.998	0.07	83.6	120.1	0.51	102	4.5
1,2,4-Trichlorobenzene	0.998	0.10	70.0	119.3	0.47	95	6.6
Naphthalene	0.997	0.05	77.5	104.4	0.45	91	3.8
1,2,3-Trichlorobenzene	0.998	0.07	78.1	114.1	0.48	96	4.8

1. Quadratic curve with 1/X weighting.
2. %RSD of the peak areas for the internal standard or the calculated amount for the surrogate standards from the calibration curve samples.
3. %RSD of the peak areas for the internal standard or the calculated amount for the surrogate standards from the seven MDL samples.
4. Mass ion 49 used.

**Figure 1** Primary Characteristic Ions for the First Seven Gases of a 0.2 ppb Standard Indicating Excellent Detection Limits with Minimal Interference from Water.



**Figure 2** Total Ion Chromatogram of a 5 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds with No Water Interference.



## Conclusion

The Teledyne Tekmar Lumin purge and trap concentrator and AQUATEk 100 was used to process water samples containing VOCs following US EPA Method 524.4 with detection by a Thermo Scientific TRACE 1310 GC and ISQ LT MS system. The linearity of the calibration curve from 0.2 ppb to 50 ppb passed all method requirements with no interference from excessive water. The MDL, precision and accuracy for seven 0.5 ppb standards also indicated no interference from excessive water.

## References

1. *Method 524.4 - Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas*; US EPA, Office of Water, May 2013.